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Highly Refined Mineral Oils

Ronald A. Phillipps
Ronald A. Phillipps & Associates
Oxfordshire, England

I. INTRODUCTION

This chapter is prepared such that it can be understood readily by the nonexpert. It is assumed that the reader has minimal knowledge of the chemistry of crude petroleum and petroleum products, and of the refinery processes involved in the manufacture. Readers who are quite familiar with these areas may wish to skip Sections II and/or III.

II. BASIC CHEMISTRY OF CRUDE PETROLEUM

A. General

"Crude petroleum" is the expression used to describe the liquid that emanates directly from the oil well. Gases also emanate from the well, because the reduction in pressure that occurs upon drilling allows some of the gases that had been trapped in the liquid to come out of solution. These gases are either flared off, or with the more environmentally aware attitudes now prevailing, are processed for transportation to industrial or domestic consumers.

The liquid comprises a range of materials, predominantly molecules containing carbon and hydrogen. There are molecules containing nitrogen, sulfur, and to a lesser extent oxygen and metals, as well as the carbon and hydrogen.

The molecules range from the most simple hydrocarbon, which is methane (CH_4), up to extremely complex molecules containing many hundreds of carbon atoms. The different materials have boiling points at normal atmospheric pressure ranging from −161°C for methane to 400°C and beyond. In fact many of the materials will not vaporize at all at normal atmospheric pressure but thermally degrade or "crack" at temperatures higher than approximately 350–400°C.

The bonding of the carbon and hydrogen atoms in the hydrocarbon molecule can be shown pictorially. A carbon atom is connected to other atoms in the hydrocarbon molecule by four "arms" or bonds. The chemical expression for this is that carbon has a valence of 4. Hydrogen

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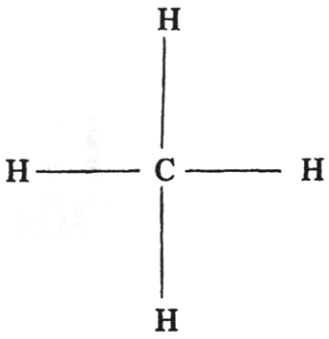

Figure 1 Structure of methane molecule, CH_4.

is connected to other atoms in the hydrocarbon molecule by only one bond; that is, hydrogen has a valence of 1. It is thus possible to depict the structure of a methane molecule according to the scheme in Fig. 1.

B. Paraffins

The hydrocarbon molecule containing two carbon atoms is entitled ethane, and the molecule with three carbon atoms is entitled propane (Figs. 2 and 3). The hydrocarbon containing four

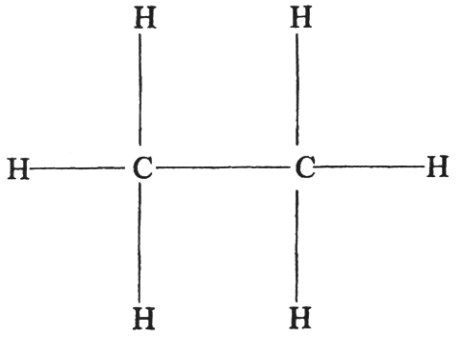

Figure 2 Structure of ethane molecule, C_2H_6.

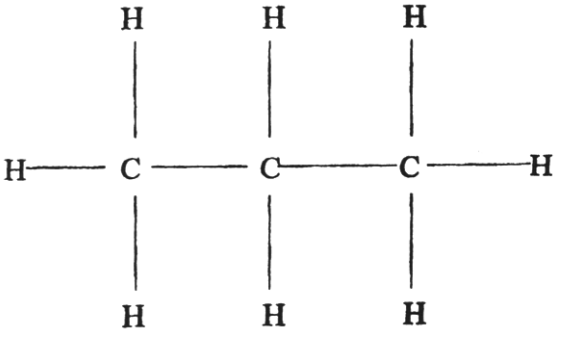

Figure 3 Structure of propane molecule, C_3H_8.

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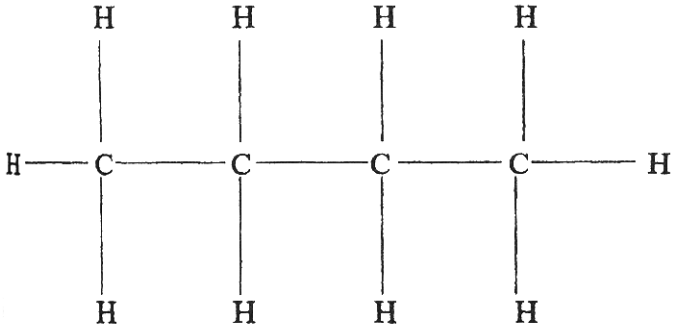

Figure 4 Structure of butane molecule, C_4H_{10}.

carbon atoms is entitled butane (Fig. 4). It will be noted that in all these examples, each carbon has four bonds, linking it to neighboring atoms, and each hydrogen has one bond, linking it to a single neighboring atom.

Similar structures exist for the molecules containing greater numbers of carbon atoms. A molecule with five carbons is entitled pentane, one with six is entitled hexane, and longer chains of carbon are called in general by the appropriate Latin-derived name. This family of hydrocarbons is entitled paraffins.

The molecules considered so far have had the carbon atoms in a straight line, and thus they are called straight chain paraffins or normal paraffins, often abbreviated to *n*-paraffins. There are hydrocarbon molecules comprising branched chains of carbon atoms, the so-called branched chain paraffins, or isoparaffins. Isobutane, which can be illustrated as shown in Fig. 5, is an example of an isoparaffin. Again, it is to be noted that each carbon is linked to its neighbors with four bonds and each hydrogen is linked to one neighbor with one bond.

Note that the isoparaffin has the same number of hydrogen atoms as the straight chain paraffin of the same carbon number. Note also that it is not possible to have a greater number of hydrogen atoms for a given carbon number than are present in these paraffinic molecules.

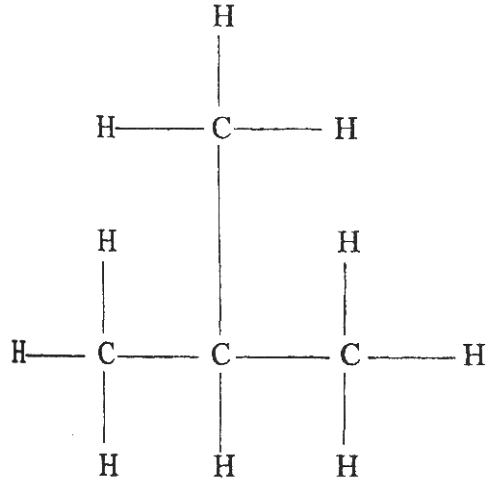

Figure 5 Structure of isobutane molecule, C_4H_{10}.

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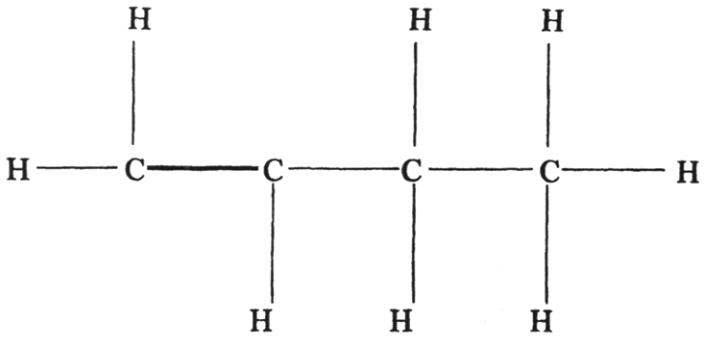

Figure 6 Structure of 1-butene molecule, C_4H_8.

For this reason, the paraffins are said to be saturated. All the straight chain and branched chain paraffins can be seen to fit the general formula C_nH_{2n+2}.

C. Olefins

There is a family of hydrocarbons in which some of the carbon atoms are associated more closely with a neighbor. That is, a carbon atom will link with a neighboring carbon atom with a double-bond link. Such hydrocarbons are entitled olefins. As with the paraffins, olefins can have either a straight chain of carbon atoms or a branched chain of carbons.

An example of a straight chain olefin is 1-butene, the "1-" indicating that the double bond is at the first position in the carbon chain (Fig. 6). 2-Butene is a similar molecule, but with the double bond in the second position in the carbon chain. The 1- and 2-butenes are often referred to generically as butenes or butylenes.

Isobutylene (Fig. 7) is an example of a branched chain olefin. Note that each carbon is still linked to its neighbors with four bonds, although one of the links is by a double bond.

It is interesting to note the differences between the butane and butylene. To accommodate the double-bond link and still retain the requirement that each carbon be linked to its neighbors

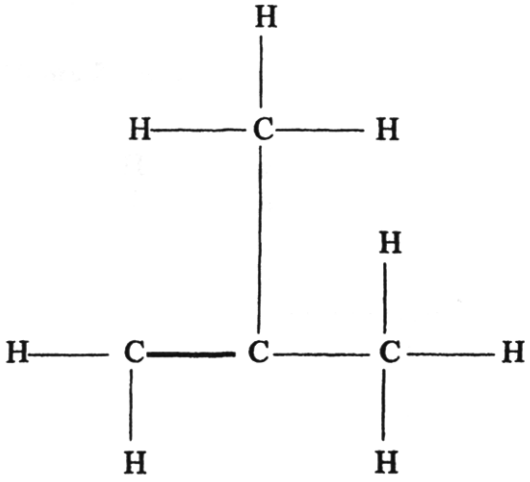

Figure 7 Structure of isobutylene molecule, C_4H_8.

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by four bonds, the butylene molecule contains two fewer hydrogen atoms than the butane molecule.

Some hydrocarbon molecules contain more than one double bond. With two sets of double bonds, the material is called a diolefin. The position of the double bond is also of interest. If the double bond is connecting the end carbon to the penultimate carbon, the material is called a l-olefin, or more normally an α-olefin, because the double bond is in the first or alpha position. These materials are of particular interest because a number of molecules can be joined together, or polymerized to use the correct expression, to form a poly(α-olefin) (PAO). This family of hydrocarbons is of great significance to the lubricants industry, as discussed elsewhere in this book (see Chapter 1). An olefin molecule, which contains fewer hydrogens than the paraffin having the same carbon number, is said to be unsaturated, because it is possible to incorporate additional hydrogen atoms into the olefin molecule.

D. Cycloparaffins or Naphthenes

So far we have discussed molecules in which the carbon atoms lie in straight chains or branched chains. In other hydrocarbons, the carbon atoms form a closed ring, or in fact more than one ring. If each ring contains carbons linked to its neighbor with a single bond (i.e., there are no double bonds), the hydrocarbon is said to be a cycloparaffin or, more usually, a naphthene. An example of a naphthene is cyclohexane (Fig. 8).

E. Aromatics

If the ring contains carbons linked to their neighbors with some double bonds, the hydrocarbon is said to be an aromatic. An example of such a hydrocarbon is benzene (Fig. 9).

The more complex molecules, containing a substantial number of carbon atoms, can comprise single- and multiring structures with a number of side chains, which may be straight or branched. These are still classed as naphthenes or aromatics depending on whether they contain any double bonds in the ring structures, as defined above.

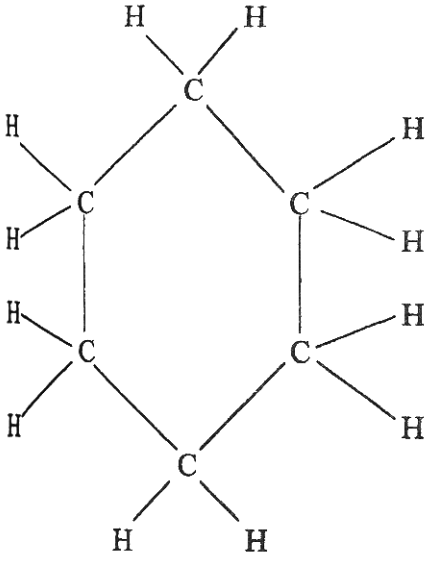

Figure 8 Structure of cyclohexane molecule, C_6H_{12}.

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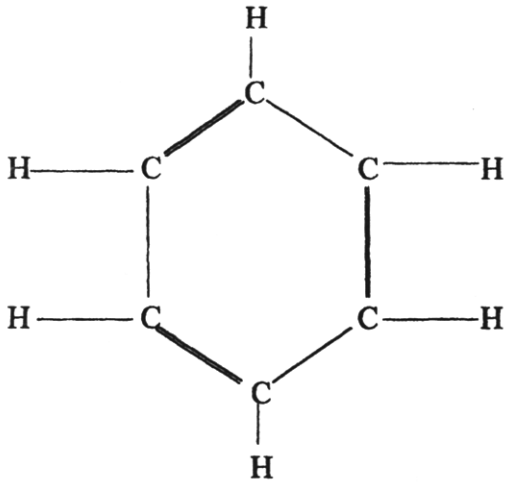

Figure 9 Structure of benzene molecule, C_6H_6.

Because aromatic structures by definition contain double bonds, they contain fewer hydrogen atoms than the naphthenic molecules having the same carbon number. They are therefore also said to be unsaturated in that they could incorporate additional hydrogen atoms.

F. Summary of Hydrocarbon Structures

We thus have the four families of hydrocarbons:

paraffins, both straight and branched chain
olefins, both straight and branched chain
naphthenes
aromatics

As stated earlier, crude petroleum contains numerous hydrocarbons, some of which have hundreds of carbon atoms in their structure. Only the simpler hydrocarbons were discussed above, but the same general principles apply to the structures of the more complex molecules. We have already stated that some of the molecules contain sulfur and nitrogen atoms, and to a lesser extent oxygen and metals, but it is beyond the purpose of this chapter to review these structures in detail.

III. REFINING OF CRUDE PETROLEUM

A. Primary Distillation

The different hydrocarbons boil at different temperatures: the larger the molecule, the higher the boiling point. For example, at normal atmospheric pressure, methane boils at −161°C, ethane at −88°C, propane at −42°C, butane at 0°C. Dodecane, a paraffin containing 12 carbon atoms, boils at 214°C, and the molecules with even greater numbers of carbons boil at ever increasing temperatures.

The isomers boil at temperatures slightly lower than the straight chain hydrocarbons having the same number of carbon atoms, or carbon number, to use the more scientific expression. For example, isobutane boils at −10°C compared to the 0°C for *n*-butane.

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Olefins boil at broadly similar temperatures to the corresponding *n*-paraffins. For example, butylene boils at between −5°C and +3°C depending on the location of the double bond, versus the 0°C boiling point of *n*-butane, which has the same carbon number. To complete the patten for the C_4 hydrocarbons, isobutylene boils at −6°C.

Since the different hydrocarbons boil at different temperatures, it is possible to separate the crude petroleum into different fractions by distillation. This is carried out in a primary distillation column. The chemical plant required to perform the process comprises a furnace to heat the crude petroleum, maintained at a pressure slightly above atmospheric pressure, to approximately 350–400°C. The temperature selected depends on the type of crude and the relative proportions of the different fractions required. The heated crude is passed to a distillation column.

The distillation column, a long cylindrical shell mounted vertically, is fitted with a series of trays in which liquid product can collect. The hydrocarbon molecules with boiling points lower than the 350–400°C input temperature of the crude vaporize on entry into the distillation column, and the vapors rise up the column. Along the length of the column there is a temperature gradient, which exists basically because the top of the column is remote from the point of injection of the heated crude petroleum.

The trays are perforated to allow the vapors to pass through, with each perforation compris ing a riser and a bubble cap, designed to force vapors rising up the column to bubble through any liquids that have collected in the trays. This means that the vapors rise up the column until they reach a temperature (i.e., a tray) at which they will condense to form a liquid.

Products are extracted from the trays. The properties of these offtake streams can be controlled by returning some of the stream into the distillation column. The aim of the primary distillation process is to have a continuous flow of vapors up the column passing through a flow of liquid that travels down the column.

The temperature gradient, hence the temperature of each of the trays, can be controlled by adjusting the quantity and temperature of the reflux and side-stripper return streams.

The reflux is product derived from the vapors that have passed through the column without condensing on any of the trays. The fraction exiting the top of the column contains the simple hydrocarbons that are gaseous at normal ambient temperature and pressure (i.e., methane, ethane-propane, and butane) plus the gasoline fraction. The gasoline fraction is condensed from this stream by cooling the product to near ambient temperature, leaving the gases to be processed by means of other processes, and some of it is returned to the primary distillation column as the so-called reflux stream.

The side-stripper return streams are derived from the streams extracted from the trays of the distillation column. Product extracted from a tray in the column is subjected to further separation by heating with steam to raise its temperature, whereupon the vaporized fraction is returned to the main distillation column at a point higher up the column, hence at a lower temperature, than the tray from which it was extracted. This sequence causes some of the components to condense and fall back down the column. The components not vaporized by the steam heating are the offtakes from the column and are the base materials for gasoline, kerosene, and auto-diesel fuel, and so on.

It is not necessary to separate each individual hydrocarbon in the distillation process, and in fact this would be impossible because crude petroleum contains thousands of different materials. Since, in any event, only some of the various fractions have applications, the crude is split into fractions that boil over a certain temperature range. For example, the gasoline (petrol) fraction boils over the range from approximately 35 to 200°C, the aviation kerosene fraction boils over the range of approximately 150–250°C, and the auto-diesel fraction boils over the range of approximately 180–350°C.

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Note that there is significant overlap of the boiling points of the components in the three product streams just identified. There are two causes of this effect. First, a proportion of a low boiling point material will stay in solution in a higher boiling point component because it will cease to come out of solution once the concentration of vapor of that low-boiling component above the liquid has resulted in a partial pressure such that no more of the low-boiling material will evaporate. Second, there is imperfect separation of the various components because of the high flow rate through the primary distillation column.

If required, the distillate fractions from the primary distillation column can be split further into narrow boiling range materials by treatment in other distillation columns. In this way, pure chemicals can be produced for industrial plants, laboratories, and other enterprises requiring solvents.

We have not yet considered the portion of the crude that does not vaporize at all in the primary distillation column but falls to the lower part of the column as a liquid called the residue. This is the portion of interest for the manufacture of lubricants.

B. Vacuum Distillation

As already stated., one cannot heat the crude to temperatures much higher than around 350–400°C. Otherwise thermal degradation or cracking of the complex multicarbon molecules will occur. How can one separate these hydrocarbons into different fractions? The answer is to use partial vacuum.

A material boils at a temperature such that the vapor pressure is the same as the pressure under which the material is held. This means that if the process pressure is reduced, some of the materials in the residue will boil at temperatures not exceeding the 350°C or so at which degradation would take place.

The residue is therefore treated in a vacuum distillation column, which operates in exactly the same manner as the primary distillation column. However, the side streams extracted from the vacuum distillation column have increased numbers of carbon atoms, and some of them are useful components for lubricating oils. There is still a residue from the vacuum distillation column; that is, not all the crude will evaporate, even under the vacuum conditions in this column. These are molecules with even greater numbers of carbon atoms. The residue is generally the basis of heavy fuel oil and asphalt or bitumen, but it does contain materials of interest as lubricants.

The further treatment of these vacuum distillation streams is discussed in Section VI, Conventional Treatment of Streams from the Vacuum Distillation Column.

IV. DESIRABLE PROPERTIES OF LUBRICATING OILS

Before considering the further treatment performed on the side streams and residue from the vacuum distillation column, we shall discuss the desirable properties of lubricating oils. We can then show how the various treatment processes provide these properties.

A. General Requirements

The basic functions of a lubricating oil are to reduce friction and drag between two surfaces where one surface is sliding relative to the other, and to protect the sliding surfaces from corrosion. These functions, in turn, are accomplished by means of other functions, as follows.

Surfaces are never completely smooth but comprise peaks and valleys, and the lubricant fills the valleys and forms a film separating the two sliding surfaces from each other. If the peaks or asperities of one surface touch those of the other surface, local welding may occur.

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The lubricant functions to prevent, or at least minimize, such unwanted joining, thus reducing damage or wear to the sliding surfaces. A constant supply of lubricant to and away from the two surfaces will serve to remove the heat generated by friction.

It is not possible to ensure complete separation of the two sliding surfaces at all times (e.g., when the surfaces first start to move relative to each other), so some wear will occur. A flow of lubricant through the contact zone will assist in the removal of wear debris. Also once a lubricating oil is in use, some degradation of the lubricant occurs, and carbonaceous materials form. The flow of lubricant assists in the removal of these degradation products from the surfaces of the equipment being lubricated. The carbonaceous material, and wear debris, can be removed from the circulating oil by means of filtration.

The foregoing desirable functions can be achieved by careful selection of the physical and chemical properties of the lubricating oil, as discussed below.

B. Viscosity

Viscosity is a measure of the resistance to flow. It is caused by intermolecular forces resisting the movement of one molecule relative to its neighbors. The resistive force depends on the viscosity of the fluid, the velocity of one plane in the fluid relative to another plane, and the distance apart of the two planes. The viscous force can thus be expressed:

$$F = \text{viscosity} \times A \times \frac{V}{d}$$

where F is the force, in newtons, V is the relative velocity, in meters per second, A is the area of each of the plane surfaces, in square meters, and d is the distance apart, in meters. This value, F, is referred to as the absolute or dynamic viscosity. The unit of measurement, using the SI system of units, is obviously the newton-second per square meter, $[(N \cdot s)/m^2]$. Because newtons per square meter equals pascals (Pa), this unit can be simplified to pascal-seconds (Pa · s).

However, the SI unit does not have widespread use in the lubricants industry. Absolute viscosity was originally defined in the centimeter-gram-second (cgs) system of units and was defined as above but with planes of one square centimeter, one centimeter apart, moving at a relative velocity of one centimeter per second. This absolute unit of viscosity was entitled the poise, and the following exact relationship exists between the poise and the pascal-second:

$$1 \text{ Pa} \cdot \text{s} = 10 \text{ poise}$$

However, there has historically been widespread use of the unit of one-hundredth of a poise, or centipoise (cP). There is also an exact relationship between the centipoise and the pascal-second:

$$1 \text{ Pa} \cdot \text{s} = 1000 \text{ cP}$$

This leads to the useful relationship that one centipoise equals one millipascal-second (mPa · s). The latter unit does have widespread use in continental Europe, in particular in Germany and France. In France, the pascal-second has been allocated the title of poiseuille (PI), with the millipoiseuille being exactly equal to one centipoise, but this convention has yet to gain usage outside France.

The absolute viscosity is of relevance in considerations of the movement of one surface relative to another at low speeds—that is, when the asperities on the two surfaces may contact each other. This situation is referred to as "boundary lubrication."

At higher speeds, the surfaces will become separated by a film of fluid generated by the

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relative motion of the two surfaces. Under these conditions, the dynamics of the oil itself become important; this condition is referred to as hydrodynamic lubrication. Obviously, the viscous forces have a larger effect on a fluid of low density than on one of high density. It is therefore useful to have a measure of the viscosity taking into account the density of the fluid. This is obtained by having a measurement of viscosity entitled the kinematic viscosity, which is equal to the absolute viscosity divided by the density.

The unit of measurement of kinematic viscosity will be seen to be:

$$\frac{(\mathrm{N}\cdot\mathrm{s})/\mathrm{m}^2}{\mathrm{kg}/\mathrm{m}^3} = \mathrm{N}\cdot\mathrm{s}\cdot\mathrm{m}/\mathrm{kg}$$

Because the dimensions of a newton are $(\mathrm{kg}\cdot\mathrm{m})/\mathrm{s}^2$, this reduces to m^2/s. The more usefully sized unit is in one-millionth of this and is mm^2/s.

As with absolute viscosity, dynamic viscosity was originally defined in terms of the cgs system of units, and the absolute viscosity in poise divided by the density in grams per cubic centimeter was entitled the stoke, one-hundredth of which is a centistoke (cSt). Fortunately, 1 mm^2/s is exactly equal to 1 cSt. The SI unit of mm^2 units has widespread use in industry, but kinematic viscosities are still often referred to in centistokes.

Viscosity is reduced as temperature is increased. Viscosity also increases with large increases in pressure, which has the advantage of minimizing, under boundary lubrication conditions, the peak-to-peak contact and wear referred to above. The effect of increasing pressure on viscosity is significant only at the very high pressures that occur when the two sliding surfaces are in very close proximity to each other; there is no measurable effect at other conditions.

Viscosity is of prime importance. For all applications, the viscosity of the lubricant must permit the oil to flow to the surfaces to be lubricated, and an oil film thick enough to prevent excessive wear must be maintained. Equipment usually operates over a range of temperatures: the equipment is started from rest at ambient temperature but the normal operating temperatures, reached after the equipment has been running for some time, will be higher than the surroundings.

Ambient temperature can itself range from low temperatures (e.g., for equipment standing overnight in adverse weather conditions) to extremely low temperatures (e.g., for equipment operated in space, on satellites).

The normal operating temperature can also range from fairly modest temperatures for equipment operating at slow speeds (e.g., slewing gears on earthmoving machinery or tank turrets) to high temperatures for equipment operating at high speeds, where the removal of heat from the lubricated surfaces is difficult because the surrounding temperatures are high. In gas turbine bearings, for example, the bearing chamber may be completely surrounded by hot products of combustion.

As already stated, lubricating oils, like other liquids, tend to thin out when heated and to thicken when cooled. However, oils vary in their response to change in temperature depending on the chemical structure of the oil.

C. Variation of Viscosity with Temperature: Viscosity Index

It is well known that certain equipment, which is started up from low temperatures, subsequently must operate at high temperatures. Examples include automotive or aircraft engines operating in arctic conditions, where they may soak overnight in temperatures as low as −50°C, with the oil during daytime operation required to lubricate bearings at 200°C or more. Such an environment requires a lubricant that will undergo only a small variation in viscosity as the temperature increases.

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In the development of lubricating oils, it was found that lubricants manufactured from Pennsylvanian crudes had the smallest reduction in viscosity as temperature was increased, while those manufactured from hydrocarbons extracted from the Gulf of Mexico were found to have the greatest variation with temperature. The variation with temperature was entitled viscosity index, almost universally abbreviated to VI.

A lubricant derived from a Pennsylvanian crude was arbitrarily designated 100 VI, while one derived from a Gulf crude was designated 0 (zero) VI. The Pennsylvanian-derived lubricants comprised hydrocarbons that were predominantly paraffinic, while those derived from Gulf crudes were predominantly naphthenic.

The VI of any lubricant can be determined by means of tables and charts according to the American Society for Testing and Materials (ASTM) Method D-2270, which is jointed to (i.e., identical to) the Institute of Petroleum (IP) Method 226. It is also jointed to ISO Method 2909.

Advanced treatment methods for lubricating oils, and the inclusion of additives, have resulted in lubricants of VI up to and beyond 400.

D. Cloud Point

If a lubricating oil is cooled sufficiently, a temperature will be reached at which wax crystals start to form in the oil. The temperature at which wax crystals first start to appear is entitled the cloud point. Cloud point determinations are made according to ASTM D-2500, which is jointed to IP 219 and ISO 3015.

We have mentioned that branched chain paraffins have a lower boiling point than normal paraffins. There is a similar effect with respect to freezing point. The branched chain paraffins have a significantly lower freeze point than the normal paraffins, making the branched chain paraffins much more suitable for use as lubricants capable of operating at low temperatures than normal paraffins of the same carbon number.

E. Pour Point

If a lubricating oil is cooled sufficiently, a temperature will be reached at which the oil will flow under the influence of gravity extremely slowly. This happens either when the oil becomes too viscous to flow appreciably or when wax crystals form. The temperature at which the oil is on the point of ceasing to flow according to rigidly defined test conditions is entitled the pour point. Pour point determinations are made according to ASTM D-97, which is jointed to IP 15. As yet, there is not an agreed ISO method.

F. Oxidation Stability

The hydrocarbon molecules react with atmospheric oxygen and this causes degradation of the oil. The reaction is accelerated by:

increased temperature
the presence of a catalyst, particularly copper or iron
the presence of water
the presence of acids, particularly resulting from oxidation/degradation of the oil
solid contaminants, particularly carbonaceous materials resulting from oxidation of the oil

Once the oxidation process has commenced, the foregoing factors ensure that the rate of oxidation and degradation will increase with time.

There are two types of material produced by this oxidation process. One can have either or both of the following:

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oil-insoluble materials, that is, oil-insoluble resins, varnishes, and sludge
oil-soluble material, that is, soluble /resins, organic acids, and peroxides

Paraffinic oils are more resistant to the oxidation process than naphthenic oils. However, naphthenic oils tend to form carbonaceous deposits, which are not as hard as those formed from paraffinic oils. This advantage means that deposits may be more readily removed from the oil-wetted surfaces of equipment, or in fact more resistant to being laid down in the first place. Aromatics also have poor oxidation stability relative to paraffins.

The effects of the oil oxidation process are manyfold. First, the resins formed in the oil increase the viscosity. Second, any acids formed will tend to corrode the metal surfaces they contact. Third, the sludges formed will be laid down in the oil system, with the particular risk that they may cause the blocking of oilways feeding the oil to the areas of the equipment that need lubricating.

There are a number of tests to assess the performance of an oil with regard to its resistance to oxidation, but these generally do not correlate well with the performance of the oil in actual use in engines and other equipment. For this reason, the resistance to oxidation in a specific application can be confirmed only by engine or rig tests, and eventually by performance in the actual equipment in the type of service in which it is to be used.

G. Evaporative Loss

We have shown how the different hydrocarbons have different boiling points and can be separated by distillation. The same process can occur in high temperature equipment, where the more volatile components can be vaporized and lost via vents from the oil system. Increasing demands for the minimization of oil consumption have resulted from demands that intervals between servicing be increased. This has led to demands, particularly from the automotive industry, for oils with minimal evaporative loss.

In the United States, evaporative loss is determined according to ASTM D-972.

In Europe, there is an oil-automotive industry organization concerned with the development of test procedures for the checking of the performance of fuels and lubricants in engines. This body, entitled the Coordinating European Council (CEC), has developed a test to quantify the evaporative loss of lubricants in engines. Referenced as CEC L-40-A-93, this assay is the so-called NOACK test. Evaporative loss as determined by this test is of great significance in Europe.

H. Chemical Stability/Biological Activity

Certain applications call for the highest standards of purity, chemical stability, and lack of biological activity. Medical-grade white mineral oils are used for cosmetics and in the food processing industry, where they come into direct contact with food (e.g., the coating of pans in which bread is baked and aluminum foil roll oils). Oils for these applications will meet U.S. Food and Drug Administration (FDA) standards as detailed in the Code of Federal Regulations [21 CFR 172.878 and 178.3620(a)], as well as any other local standards and regulations. Oils meeting these requirements are severely processed to ensure that all the aromatic compounds have been extracted and that the oils themselves are completely saturated. This processing is by means of acid and clay treatment, and solvent extraction of aromatics as described in Section VI. In this way chemical stability and absence of any biological activity is assured.

There is also a requirement for oils used on food processing equipment, where the oil should not normally come into contact with the food. These technical-grade white mineral oils are required to meet FDA Regulation 21 [CFR 178.3620(b)], as well as any other local requirements.

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Oils meeting these requirements are also severely processed with regard to the removal of aromatics, and so on, but to slightly lower standards than the medical grades demand.

V. ADDITIVES

While the base oils can usefully be selected to possess many of the desirable properties identified above, the properties can be enhanced significantly by the incorporation of chemical additives. It is beyond the purpose of this chapter to discuss these agents in detail, but additives can be included, depending on the application, to confer the following benefits:

Additives	Benefits
VI improvers	To improve the VI of the oil. VI as high as 400 can be obtained by means of suitable additives.
Antioxidants	To make the oil more resistant to degradation under high temperature conditions.
Dispersants	To maintain particulates (e,g., wear debris and carbonaceous materials formed by oxidation of the oil) as a finely divided suspension, thus minimizing their deposition on the oil-wetted surfaces of equipment.
Detergents	To minimize the laying down of deposits on the oil-wetted surfaces of equipment.
Antiwear	To prevent the localized welding that would occur in the absence of these materials, that chemically react with the metal surfaces when asperities of one surface meet those of another.
Rust inhibitors	To minimize the corrosion of iron/steel components in the equipment.
Antifoam	To prevent the oil from forming a foam during the churning that takes place in equipment operating at high speeds. If foam is formed, it is likely to be expelled from the equipment via vents from the oil system, resulting in loss of oil.
Demulsifiers	To prevent the oil and water that gets into the oil system (e.g., during low temperature operation) from forming an oil/water emulsion. Such an emulsion could hinder the desired flow of oil to the surfaces required to be lubricated, leading to equipment failure.

VI. CONVENTIONAL TREATMENT OF STREAMS FROM THE VACUUM DISTILLATION COLUMN

A. General

Each vacuum distillate side stream will contain hydrocarbons comprising a range of carbon number. These substances were historically classified according to their viscosity measured by means of a Saybolt Universal Viscometer at 100°F (a measurement of temperature historically used in the oil industry, although there are moves toward adopting the Celsius scale used by most countries outside the United States). The viscosity is determined by allowing a prescribed quantity of oil to flow from a vessel, maintained at the specified temperature, through a hole or orifice in its base. Obviously the time to flow through the orifice depends on the viscosity of the oil; it is reported in Saybolt Universal Seconds (SUS).

Because the density of the oil obviously plays a part in this process, with more dense oils tending to flow more readily through the hole than oils low in density, this time relates to the kinematic viscosity as discussed in Section IV. B. The Saybolt equipment and method are no longer in use, but industry still often prefers to refer to the viscosity of the base oils by SUS

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at 100°F numbers. ASTM therefore introduced conversion tables to convert SUS to mm^2/s and vice versa (see ASTM D-2161). The lubricating oil manufacturers now measure the viscosity of base oils using the current method, ASTM D-445, which is jointed to IP 71. As yet, there is no agreed ISO test method.

The viscosities of side streams from conventional refinery vacuum distillation columns will range from approximately 50 SUS to 600 SUS at 100°F, that is, approximately 7–130 mm^2/s at 40°C.

The side streams contain straight and branched chain paraffins, straight and branched chain olefins, naphthenes, and aromatic components. Components containing double bonds are inherently less thermally stable than components containing only single bonds. These streams can therefore be subjected to some of the following treatments.

B. Acid Treatment

The oil is treated with approximately 95–98% strength sulfuric acid at approximately 35–65°C in a reactor vessel heated with steam coils. This process removes components with poor oxidation stability. The contact time is kept short to minimize undesirable chemical reactions. After agitation and air blowing, the oil/acid mix is transferred to a settling tank, where the acid sludge separates by gravity. More modern plants incorporate centrifugal separation of the sludge from the oil/acid mix. Acid treatment is normally followed by clay treatment.

For the manufacture of special products like transformer oil and medical-grade and technical-grade white mineral oils, which require extremely high levels of stability and purity, oleum (strong sulfuric acid containing free sulfur trioxide) is necessary, followed by alkali washing to neutralize the lubricant.

Because of environmental difficulties in the disposal of the waste acid sludge, acid treatment is now used only for the specialist oils like transformer oils and medicinal- and technical-grade white mineral oils.

C. Clay Treatment

Acid-treated oils are given a final treatment with clay, sometimes referred to as fuller's earth, to improve the color and stability by removing traces of unstable and colored compounds still present, and to absorb traces of acid sludge and reaction products from the previous acid treatment. The oil is brought into contact with the clay and, after the reaction has been completed, the clay is removed by filtration.

D. Dewaxing

As already stated, the lubricant streams from the vacuum distillation column contain straight chain paraffins. The components containing more than 10–15 carbon atoms are in fact paraffin wax, and they readily separate from the oil by crystallization at moderately low temperatures. For example, the straight chain molecule dodecane, which contains 12 carbon atoms, solidifies at −12°C, and the straight chain paraffin pentadecane, containing 15 carbon atoms, freezes at 10°C. These molecules need to be removed to prevent the oil from precipitating wax crystals at moderately low temperatures, a development that would adversely affect the low temperature performance of the oil.

Historically the unwanted components were removed, by cooling the oil and filtering out the wax crystals in presses. There are two disadvantages to this process.

First, the viscosity of the oil is increased at the low temperature needed to extract the wax, which hinders the filtration process. This is particularly true for the heavier, more viscous oils

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from the side streams of the vacuum distillation process, although the problem could be alleviated by diluting the oil with a solvent, which could be recovered after the wax separation process. The residue from the vacuum distillation unit is virtually untreatable. This is not only because of the high viscosity of the residue, but also because the residue contains wax whose crystals are of microscopic size. This so-called microcrystalline wax cannot be removed by filtration because the crystals are so small that many of them would pass through the filter medium.

Second, this process is labor intensive, because of the need to manually handle the wax removed from the filter presses.

Therefore, the use of filter presses has been superseded by solvent dewaxing. A solvent, or often a mixture of two solvents, is added to the oil to obtain a mixture with a low viscosity at the chilling temperature and a good separation of all types of wax in a form suitable for efficient filtration. The low viscosity allows the filter press to be replaced by the more efficient rotary vacuum filter, which consists of a rotary drum with a fine mesh filter screen. The drum is made to rotate with its lower portion immersed in the oil/solvent mixture. By a system of ports, a partial vacuum is applied to the inner portion of the drum, causing the oil/solvent mixture to be drawn through the mesh filter. As the mixture passes through the filter, the wax crystals are separated out. As the drum rotates, and the cake of wax exits the oil/solvent mixture, the cake is solvent-washed to remove any oil, with the solvent passing through the filter mesh screen. This solvent is ducted away from the internal components of the drum, again by means of a port on the end plate of the drum.

Further rotation brings the wax cake to a region where another port on the end plate of the drum allows a low pressure to be applied to the wax cake, partially lifting it away from the filter mesh. The wax cake is finally removed from the filter mesh by means of a scraper to be processed for other applications—for example, the manufacture of candles or waxed paper, or as we shall see later, the manufacture of high quality base oils.

E. Solvent Extraction of Aromatic Components

The aromatic components of a lubricant are relatively unstable compared to the naphthenic and paraffinic components. They also have relatively poor viscosity index. The aromatic components can be removed by solvent extraction. Commonly used solvents are furfural, phenol, and *n*-methyl pyrolidone. The solvent extraction process also removes sulfur compounds and color bodies (i.e., materials that give the oil a dark color).

The oil is mixed with the solvent and fed into a reactor vessel maintained at around 100°C; the temperature depends on the oil to be processed and the solvent used. The solvent extract is processed to separate the aromatic components from the solvent. The solvent is reused, and the aromatic compounds extracted are processed further for use as chemical feedstocks or for inclusion in fuels.

Base oils, which have utilized solvent extraction of aromatics processes, often are referred to by their SUS viscosity and an indicator that solvent extraction has been used. For example, the 50 SUS base oil may be referred to as a 50 SN, where S stands for solvent extraction of aromatics and N indicates that the base oil has neutral acidity.

F. Hydrofining

Hydrofining, or hydrotreating, as the process may be called, is used to improve the quality of lubricant base stocks by way of the removal of sulfur, nitrogen, and other undesirable compounds. The oil is mixed with hydrogen and fed into a reactor vessel maintained at around 300°C. The sulfur is converted to hydrogen sulfide, which can be separated from the oil on exit

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from the reactor. The hydrogen sulfide can be processed to produce elemental sulfur for use in industry or agriculture, and the hydrogen reused in the hydrofining process.

Hydrofining also has the effect of saturating some of the hydrocarbon compounds; that is, it will react with the hydrocarbon and add hydrogen to the molecule, thus removing some of the double bonds referred to in Section II, Basic Chemistry of Crude Petroleum. This will improve the oxidation stability of the base oil.

G. Deasphalting

All the processes above may be used to improve the quality of the side streams from the vacuum distillation column. We have stated that the residue from the column possesses properties that are beneficial for lubricants. The residue contains materials that provide excellent film strength under boundary lubrication conditions. However, the residue is not suitable for inclusion in lubricants without some treatment. It has already been stated that the residue can form the basis for heavy fuel and bitumen or asphalt.

The asphaltine compounds in particular are not suitable for inclusion and must be removed. This is carried out by mixing the residue with liquid propane under pressure. The propane preferentially extracts the asphalt fractions and the mixture separates into two phases. One phase contains the deasphalted oil, and the other phase contains the asphalt in solution in the propane. The propane is extracted from the propane–asphalt phase by evaporation and steam stripping to recover the propane for reuse.

The deasphalted oil can be processed further by hydrofining, dewaxing, and solvent extraction of aromatics, as discussed above.

Base oils prepared in this way are referred to as "brightstock," a name given because of the sheen normally exhibited by such oils. Brightstocks have much higher viscosities than the base oils derived from the side streams of the vacuum distillation unit. It was thus not possible to measure their viscosity in the Saybolt Universal Viscometer, and so the Saybolt Furol Viscometer (a vessel with a larger diameter orifice through which the oil flowed) was used. Also, to achieve a more workable time for the vessel to empty, the viscosity was normally measured at 122°F (50°C). The viscosity was reported as Saybolt Furol Seconds (SFS), and brightstock oils are often referred to by their SFS viscosity. For example, a 175 Brightstock would have a viscosity of 175 SFS at 122°F, which is equivalent to a viscosity at 40°C of approximately 700 mm^2/s.

Not all base oil manufacturers follow this system, and the only way to know the properties of any base oil is from analysis, and not from the title.

The processes described above have been the basis of the refining of high quality lubricants for many years. However, the demand for lubricants of ever increasing performance has led to the introduction of other processes, which are described in the final section, Hydrocracking and Hydroisomerization.

VII. HYDROCRACKING AND HYDROISOMERIZATION

A. Introduction

The processes of hydrocracking and hydroisomerization were introduced because of the ever increasing demand for lubricants with improved oxidation stability and higher viscosity index. This is particularly true with respect to automotive gasoline engine lubricants, where improved oxidation stability will make possible the increased service intervals now required by users. The higher VI facilitates the production of lubricants that retain adequate viscosity at the normal

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operating temperatures but lower viscosity at low temperatures (e.g., −30 to −20°C) and thus provide improved fuel economy during the cold-start and warm-up phase of operation.

There is similar pressure for improvements to transmission lubricants, and there is also a significant and growing penetration into the hydraulics, compressor, and turbine/systems lubricants business. Oils with these properties comprise predominantly branched chain paraffins and thus contain minimal quantities of naphthenic, olefinic, and aromatic components.

Before the processes are described, it is useful to introduce the broad groupings of mineral oils agreed by the American Petroleum Institute (API). This grouping is also likely to be accepted by the Additive Technical Committee (ATC), a European body comprising the manufacturers of additives used in the lubricating oil business. They have agreed three groups for mineral base oils, as follows:

Group 1. Mineral oils refined using the historical techniques (i.e., solvent extraction of aromatics, solvent dewaxing, hydrofining to reduce sulfur content). This processing produces mineral oils with sulfur levels typically greater than 0.1%. Saturates levels are 60–80%, and VI is approximately 90.

Group 2. Mildly hydrocracked mineral oils with conventional solvent extraction of aromatics, solvent dewaxing, and more severe hydrofining to reduce sulfur levels to less than 0.1% (typically 0.03%), as well as removing double bonds from some of the olefinic and aromatic compounds. Saturates levels are 95–98%, and VI is approximately 90–100.

Group 3. Severely hydrotreated mineral oils with saturates levels of some oils virtually 100%. Sulfur contents are between 0.001 and 0.01%; VI in excess of 120.

The other groups defined by API are Group 4 [poly(α-olefins)]and Group 5 (esters, polyethers, polyalkylene glycols, etc.) which are discussed in other chapters of this book.

This chapter is focused on mineral oils comprising Groups 2 and 3 of the API system.

B. The Process

The hydrotreating process involves feeding hydrogen and the base oil to be treated into a reactor vessel at high temperature and pressure. The processes are highly confidential at present and it is not possible to give details of the temperatures and pressures involved. There are three basic aims of the reaction:

First, the removal of atoms of nitrogen, sulfur, and oxygen from the hydrocarbon molecule.

Second, the opening of the aromatic and naphthenic ring structures to convert them to straight chain and branched chain compounds, and to crack the side chains on these ring-structured compounds to reduce the chain length. The process is also aimed at saturating the materials thus formed.

Third, for oils with strongly aromatic structures, the saturation to naphthenic rings of the aromatic rings (note that not all the rings are opened during this process).

Some processes, in particular the Shell XHVI (registered Shell trademark) and Exxon Exxsyn (Exxon registered trademark), convert the long straight chain (i.e., the *n*-paraffins) and the near-normal paraffins (i.e., paraffins with minimal number of side chains) to isoparaffins.

The feedstock—that is, the material to be processed—is generally a side stream from a vacuum distillation column, but it may incorporate material derived from other plants in a complex refinery. This additional material may include, for example, slack wax derived from the solvent dewaxing processes used to enhance the low temperature properties of lubricating oil base stocks.

In the case of the Shell XHVI and Exxon Exxsyn processes, the feedstock is simply the

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wax from the solvent dewaxing process alone; that is, it is not used in conjunction with any other refinery streams.

Because hydrocracking and hydroisomerization processing involves the cracking of the side chains of molecules, smaller molecules are manufactured. As discussed in Section II, these molecules will have comparatively low boiling points and are thus of no use in the manufacture of lubricants. These low-boiling materials are therefore separated from the heavier molecules in strippers and fed into the gasoline–kerosene–diesel manufacturing process.

The residue from the stripper is then fed to another vacuum distillation column, where the different lubricant fractions are extracted as side streams. These streams are treated by conventional hydrofining and solvent dewaxing to further improve base oil quality. The processes involving the conversion of normal and near-normal paraffins can utilize the waxes extracted by the solvent dewaxing process; these are fed back into the hydrocracking reaction, to produce the isoparaffins as described above.

The base oils using these processes are broadly referred to as VHVI (i.e., very high viscosity index) base oils.

Most of the world's major oil companies are producing, or are in the process of installing plant so that they can produce, these VHVI base oils. These firms include Chevron, British Petroleum, Exxon, Idemitsu, Shell, Mobil, Petro-Canada, Ssanyong, Sun Oil, Nippon Oil, Pennzoil, and Yokong. This listing is by no means definitive, as additional plant capacity is continually being considered by the industry.

C. VHVI Lubricant Product Quality

It is interesting to examine the properties of the base oils produced by these severe hydrotreating processes. Table 1 shows typical properties of some 4 mm^2/s VHVI base oils compared to the typical properties of Group 1 and Group 2 base oils. A poly(α-olefin), Amoco PA04, is included for comparison.

It will be noted that the severely hydrocracked lubricants have VI significantly better than the conventionally treated HVI base stocks of Groups 1 and 2. It will also be noted that the NOACK evaporative loss for the VHVI oils are lower than for the HVI oils.

Also to be noted are the very low sulfur levels and nitrogen contents. The aromatics contents of the VHVI oils are lower than for Group 1 oils but can in fact be higher than those for Group 2 oils, which have been subjected to severe solvent extraction of aromatics. The Shell XHVI oil is virtually 100% saturates, with no measurable aromatics.

Table 1 Physical and Chemical Properties of 4 mm^2/s VHVI Hydrocarbon Base Stocks

	HVI base stocks		PAO:	VHVI base stocks		
Property	Group 1	Group 2	Amoco PAO4	BP HC4	Texaco TexHVI	Shell XHVI
Kinematic viscosity at 100°C, mm^2/s	3.81	4.01	3.89	3.99	4.44	4
VI	92	96	124	128	127	144
Pour point, °C	−18	−12	−54	−27	−15	−18
NOACK, %	32	31	13	15.8	17	16.4
Sulfur, %	0.46	0.003	0	0.08	0.01	0.002
Nitrogen, ppm	17	5	0	2	2	2
Aromatics, %	18.2	1.1	0	7.7	6.3	0
Saturates, %	81.8	98.9	100	92.3	93.7	100

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Table 2 Physical and Chemical Properties of 5–6 mm^2/s VHVI Hydrocarbon Base Stocks

	HVI base stocks		PAO:	VHVI base stocks		
Property	Group 1	Group 2	Ethyl PAO6	BP HC6	Shell XHVI	Exxon Exxsyn
Kinematic viscosity at 100°C, mm^2/s	5.3	5.66	5.81	5.59	5.14	5.8
VI	96	97	136	130	146	142
Pour point, °C	−9	−12	−54	−12	−18	−21
NOACK, %	16	17.5	8.2	8.9	11	9
Sulfur, %	0.4	0.006	0	0.001	0.002	0.001
Nitrogen, ppm	53	5	0	5	2	0
Aromatics, %	34.9	0	0	2	0	0
Saturates, %	65.1	100	100	98	100	100

The VHVI oils are generally fairly similar to the poly(α-olefin) lubricant Amoco PA04, with the exception of pour point, where the PA04 is superior.

Table 2 shows typical properties of some 5–6 mm^2/s base oils compared to the typical properties of base oils from Groups 1 and 2; again, a poly(α-olefin), Amoco PA06, is included for comparison.

As for the 4 mm^2/s base stocks, the VHVI have superior VI, better NOACK evaporative loss, and lower aromatics than were found for Group 1 oils. It will be noted that the Shell XHVI and Exxon Exxsyn are both virtually 100% saturates with no measurable aromatics.

Another point of interest is that VHVI base oils can be manufactured by the synthesis of natural gas to wax, using the Fischer–Tropsch process. The wax can then be processed by hydroisomerization or catalytic isomerization of the wax to produce VHVI base oils.

Evaluation of these VHVI base oils shows that they exhibit excellent oxidation stability as well as the very high VI shown by the laboratory tests. Performance is comparable to that obtained by poly(α-olefins), which might be expected because of their broadly similar chemical structure, but at reduced costs of production.

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